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CHEMICAL CONSTITUENTS FROM THE LEAVES OF *CARYA ILLINOINENSIS*, AERIAL PARTS OF *HELICHRYSUM STOECHAS* AND HULLS OF *ORYZA SATIVA*

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ABSTRACT

Carya illinoinensis (Wangenh.) K.Koch (family Juglandaceae) has astringent and piscicide properties. Its bark is used to treat tuberculosis, the pulverized leaves are rubbed on the skin to cure ringworm and taken as a tea. *Helichrysum stoechas* (L.) Moench (family Asteraceae) is useful to relieve allergies, bronchitis, common colds, flu, respiratory problems and sinusitis. *Oryza sativa* L. (family Poaceae) is used as a foodstuff, medicines and cosmetics. It is taken to treat abdominal ailments, beriberi, burns, dyspepsia, epistaxis, fever, filariasis, flux, hematemesis, inflammations, jaundice, nausea, neurodegenerative diseases, ophthalmia, paralysis, piles, psoriasis, rheumatoid arthritis, skin ailments, sores, swellings and in rejuvenation therapy. Phytochemical investigation of the leaves *C. illinoinensis* gave a new dixyloside characterized as α-L-xylopyranosyl-(2→1')-α-L-xylopyranoside (**1**). The aerial parts of *H. stoechas* afforded *n*-tetracosanoic acid (lignoceric acid, **2**), lanost-5-en-3α-ol 26-oic acid (**3**), lanost-5-en-3β-olyl hexadecanoate (lanost-5-en-26-oic acid 3β-olyl palmitate, **4**) and lanostan-3α- olyl -26-oic acid 3-O-α-D-glucopyranoside (lanostan-3α- olyl -26-oic acid 3-O-α-D-glucoside, **5**). The hulls of *O. sativa* led to the isolation of an aliphatic acid identified as *n*-hexacos-14-enoic acid (**6**). Except compounds **2** and **6**, all the phytoconstituents are unknown and reported for the first time. The structures of all these compounds have been established on the basis of spectral data analyses and chemical reactions.

KEYWORDS: *Carya illinoinensis* leaves, *Helichrysum stoechas* aerial parts, *Oryza sativa* hulls, phytoconstituents, isolation, characterization.

INTRODUCTION

Carya illinoinensis (Wangenh.) K.Koch, syn. *C. angustifolia* Sweet, *C. diguetii* Dode, *C. oliviformis* (F.Michx.) Nutt. and *Juglans illinoinensis* Wangenh. (family Juglandaceae), known as pecan nut, queen of nuts, sweet pecan and Illinois nut, is a species of hickory native to northern Mexico and the southern United States, grown in Australia, Kashmir and Himachal Pradesh.[1,2] Its trunk is thick gray-brown, bark ridged, scaly; twigs are red-brown; leaves deciduous, alternate, serrate, pinnately divided into 9 – 17 oblong-lanceolate leaflets; flowers unisexual, yellow green; fruits ellipsoidal drupes, 4-winged; seed single, brown, sweet, surrounded by a thin shell. Its bark and leaves are astringent and piscicide. A decoction of the bark has been used to treat tuberculosis. The pulverized leaves are rubbed on the skin to treat ringworm and used as a tea. Its seed oil is edible.[3.4] The pecan nuts contained ellagic, gallic, protocatechuic and *p*-hydroxybenzoic acids, catechin, tannins, protocatechuic aldehyde, epigallocatechin, gallic acid-glucose conjugate and valoneic acid dilactone [5-8], lipids [9], epigallocatechin-3-gallate[10] and proteins. [11] The plant essential oil was composed mainly of camphor, l-fenchone, *cis*-carvone oxide, β-elemene, *cis*-*z*-α-bisabolene epoxide, aromadendrene, camphene, β-eudesmene and caryophyllene oxide.[12] The plant afforded phenolics, flavonoid glycosides, galloylated glycosides and condensed tannins. [13-17]

Helichrysum stoechas (L.) Moench, syn. *Gnaphalium citrinum* Lam. and *G. stoechas* L. (family Asteraceae), known as shrubby everlasting, God's flower, Gold flower, Golden stoechas, Goldylocks, is common in the Mediterranean region, north-western Africa, eastern Turkey, southern India, Sri Lanka and Australia. It is often found on uncultivated land and along roadside. This plant develops on soils with acidic, neutral, alkaline

pH and well drained sites.[18-20] It is a perennial, evergreen, compact, bushy, spreading, aromatic herb, growing up to 60 cm; stem woolly, leaves simple, alternate, linear, with entire margins; flowers umbels of yellow many-stellate foliage. It has anti-inflammatory, antifungal and antioxidant, deobstruent, expectorant, laxative and sudorific properties; used to treat allergies, bronchitis, common colds, flu, respiratory problems and sinusitis. It can be used in cooking, in meat dishes, soups, rice and as a condiment. Its essential oil has healing, anti-ageing, anti-inflammatory, hemostatic, lipolytic, and regenerating properties. The flowers are taken as a diaphoretic and discutient.[21,22]

The *H. stoechas* plant and its varieties contained essential oils composed mainly of α-pinene, limonene, α-bisabolol, β-caryophyllene, α-humulene, pinocampheol, β-elemene, benzyl benzoate, allo-aromadendrene and epi-α-bisabolol,[21,23-29] isomers of caffeoylquinic and dicaffeoyl quinic acids, their isomers, pigenin glucoside, quercetin and kaempferol,[21], neo-chlorogenic, chlorogenic and crypto-chlorogenic acids, naringenin, quercetin, kaempferol and apigenin glucosides, a tetrahydroxychalcone-glucoside,[30] arzanol, α-pyrone, helipyrone, *p*-hydroxybenzoic, caffeic and neochlorogenic acids, 5,7-dihydroxy-3,6,8-trimethoxyflavone, isoquercitrin, quercetagetin-7-*O*-glucopyranoside and santinol B.[31,32]

Oryza sativa L. (family Poaceae), commonly known as dhania and rice, is the most widely grown tropical cereal. It is used as a foodstuff, medicines and cosmetics. Rice is astringent, demulcent, diuretic, emollient, larvicidal, nutritive, refrigerant, soothing, stomachic, tonic and vermifuge. It reduces lactation, improves digestion, controls sweating and useful to treat abdominal ailments, beriberi, bowels, burns, diarrhoea, dysentery, dyspepsia, epistaxis, fever, filariasis, flux, hematemesis, inflammations, jaundice, nausea, neurodegenerative diseases, ophthalmia, paralysis, piles, psoriasis, rheumatoid arthritis, skin ailments, sores, splenosis, stomach ailments, swellings and in rejuvenation therapy. A rice paste is applied to cure boils, sores, swellings and skin blemishes. Sticky glutinous rice is taken to comfort stomach upsets, heart-burn and indigestion. A poultice of soft rice is applied to back and chest to relieve bronchitis and coughs. The rhizome is ingested to treat night sweats, tuberculosis and chronic pneumonia. Lye from burned culms is considered abortive; used as a hair wash and internally as an abortifacient. Rice water is beneficial as an enema. Hulls of mature plants are ingested against dysentery. The dried flowers are useful in cosmetic and dentifrice, awns are taken to control jaundice. The stem is used for bilious conditions; stem ash for discharges and wounds. An infusion of straw is drunk against dysentery, gout and rheumatism. The husk is considered as a tonic and administered orally to relieve dysentery. Rice cakes are fried in camel's fat and eaten to relieve piles. Rice water is drunk to relieve fluxes and ulcers and applied externally with pepper as a remedy for gout. Boiled rice is eaten to get rid of carbuncles. The root is considered astringent and anhidrotic, a root decoction is drunk to alleviate anuria. Rice sprouts are used to recover poor appetite, dyspepsia, fullness of abdomen and weak spleen. Rice bran oil has antioxidant properties that promotes cardiovascular strength by reducing cholesterol levels in the body.[33-35]

The hulls of *O. sativa* contained steroidal constituents, hentriacontane, 1-tetratriacontanol, momilactones A and B, β -sitosterol, its glucuronoside and glucoside, 3,7-dimethyl-*n*-octan-1-yl benzoate, tricin, lanostdien-3,15-diol glucoside, phenolic glucoside, orizaterpenol, orizaterpenoid, orizaterpenyl benzoate, orizanor-diterpenyl benzoate and orizaditerpenyl benzoate,[36–39] abietatrie-7-one, pimara-7,15-diene and momilactone A derivatives, ent-7-oxo-kaur-15-en-18-oic acid,[40] aliphatic alcohols and esters.[41]

The plant straw and leaves afforded flavones, kaempferol and methyl salicylate glycosides, oleioyl-β-D-arabinoside, diferuloxy feruloyl glycoside, *p*-hydroxybenzoic, vanillic, *p*-coumaric and ferulic acids, sakuranetin, glyceryl-dioleo-linoleate, fatty acid and ester.[42-46] Rice grain yielded oryzaterpenyl caffeoate and linoleic, myristic and stearic acids, [47] tricin and flavonolignans,[48] fatty acids,[49] and ethyl iso-allocholate, [50] vanillin and coumaric acid.[51] The roots furnished 2-*O*-(*E* / *Z*)-feruloyl glycerides and 8-hydroxyacacetin.[52] The rice bran possessed fatty esters,[53] palmitic acid, stigmasterol, cerotic acid, 1,2-dioleiyl-β-D-xyloside, orizatriterpenolide, oleiyl-β-D-arabinopyranoside, ricinoleic acid-5-O-β-D-glucoside,[54] oryzanols, tocopherols, tocotrienols, phytosterols, fixed oil (20 %), proteins (15 %), carbohydrates (50 %, mainly starch) dietary fibers like beta-glucan, pectin and gum.[55,56]

Keeping in view the various therapeutic values of the plants and the development of ecofriendly, biodegradable and safer herbal preparations the leaves of *Carya illinoinensis*, aerial parts of *Helichrysum stoechas* and hulls of *Oryza sativa* were screened for the isolation and characterization of their chemical constituents.

General Procedures

Melting points were measured using one end open capillary tubes on a thermoelectrically heated melting point apparatus (Perfit, India) without correction. UV spectra were determined with Lambda Bio 20 spectrophotometer (Perkin Elmer, Schwerzenbach, Switzerland) in methanol. The IR spectra were obtained by using KBr pellets on Win IR FTS 135 instrument, Biorad, USA. The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker DRX Spectrometer (Rheinstetten, 2 Germany) using $CDCl_3$ and DMSO-d_6 as solvents. TMS (Fluka analytical, Sigma-Aldrich, Netherland) was taken as an internal standard and the coupling constants (J values) are expressed in Hertz (Hz). Mass spectra were recorded by

affecting electron impact ionization at 70 eV on a Jeol - Accu TOF JMST100LC mass spectrometer equipped with direct inlet prob system. The *m/*z values of the more intense peaks are mentioned and the figures in brackets attached to each *m/*z values indicated relative intensities with respect to the base peak. Column chromatography was performed on silica gel (Qualigens, Mumbai, India) with 60-120 mesh particle size. The purity of the isolated compounds was checked on precoated TLC plates with silica gel 60 F_{254} (0.25 mm, Merck, Mumbai, India). The spots were visualized by exposure to iodine vapors and under UV radiations at 254 and 366 nm and spraying with ceric sulphate solution. The percentage yields of the isolated compounds were calculated on the basis of dried plant material (1.0 kg) taken for extraction.

Plant material

The leaves of *Carya illinoinensis* were procured from the fruit form of Palam pur, Himachal Pradesh. The hulls of *Oryza sativa* were obtained from a rice mill of Ghaziabad, Uttar Pradesh. The plant materials leaves and hulls were authenticated by Prof. M. P. Sharma, Taxonomist, Department of Botany, Jamia Hamdard, New Delhi. The voucher specimens of these plant parts are preserved in the herbarium of the Department of Pharmacognosy and Phytochemistry, Jamia Hamdard, New Delhi.

The fresh aerial parts of *Helichrysum stoechas* were collected from the basin of the Mediterranean sea, Libya. It was authenticated by Dr. Huda Elgubbi, Department of Botany, College of Science, Misurata University, Misurata, Libya. A voucher specimen No. HC 55/01 of the plant has been submitted in the herbarium, Department of Botany, College of Science, Misurata University, Misurata, Libya.

Extraction and isolation

The leaves of *C. illinoinensis*, hulls of *O. sativa* and aerial parts of *H. stoechas* (1 kg each) were dried in air, coarsely powdered and extracted separately and exhaustively with methanol in a Soxhlet apparatus. The extracts were concentrated under reduced pressure to get dark brown masses, 113.7 g, 91.2 g and 119.6 g, respectively. Each dried residue (90 g each) was dissolved in minimum amount of methanol and adsorbed on silica gel column grade (60-120 mesh) separately to obtain slurries. Each slurry was air-dried and chromatographed over silica gel columns loaded in petroleum ether (b. p. 60 – 80 °C) individually. Each column was eluted with petroleum ether, petroleum ether - chloroform (9:1, 3:1, 1:1, 1:3, *v/v*), chloroform and chloroform - methanol (99:1, 49:1, 19:1, 9:1, *v/v*). Various fractions were collected separately and matched by TLC to check homogeneity. Similar fractions having the same R_f values were combined and crystallized with solvents. The isolated compounds were recrystallized to get pure compounds.

Isolation of a phytoconstituent from the leaves of *Carya illinoinensis*

α-L-Xylopyranosyl-(2→1')-α-L-xylopyranoside (1)

Elution of the column with chloroform-methanol (9:1) afforded colourless crystals of **1**, yield 286 mg, m. p. 93 – 95 ºC; UV λmax (MeOH): 245 nm; IR υ_{max} (KBr): 3365, 3231, 2925, 2842, 1445, 1325, 1268, 1202, 1103, 1002, 819 cm^{-1}; ^{1}H NMR (MeOD): δ 4.61 (1H, d, J = 4.8 Hz, H-1α), 4.42 (1H, m, H-2), 3.70 (1H, m, H-3), 3.52 (1H, m, H-4), 3.31 (2H, d, J = 4.5 Hz, H_2-5), 4.53 (1H, d, J= 5.7 Hz, H-1' α), 4.32 (1H, m, H-2'), 3.62 (1H, m, H-3′), 3.48 (1H, m, H-4'), 3.20 (2H, d, J = 4.5 Hz, H_2-5'), ^{13}C NMR (MeOD): δ 99.17 (C-1), 79.23 (C-2), 75.37 (C-3), 72.19 (C-4), 70.84 (C-5), 93.51 (C-1′), 76.86 (C-2′), 72.57 (C-3′), 71.73 (C-4′), 70.12 (C-5′); +ve ESI MS *m/z* (rel. int.): 282 $[M]^+$ ($C_{10}H_{18}O_9$) (1.5).

Isolation of phytoconstituents from the aerial parts of *Helichrysum stoechas* Lignoceric acid (2)

Elution of the column with petroleum ether - chloroform (2:3) gave colourless crystals of **2**, recrystallized from acetone-methanol (1:1), yield 147 g, R_f 0.61 (petroleum ether - chloroform, 2:3), m. p. 83 – 84 ^{0}C; IR υ_{max} (KBr): 3409, 2923, 2856, 1690, 1461, 1383, 1231, 1176, 1148, 1037, 1003, 889, 724 cm^{-1}; ^{1}H NMR ($CDCl_3$) : δ 2.37 (1H, J = 7.3 Hz, H_2-2), 2.06 (2H, m, H_2-3), 1.63 (2H, m, H_2-4), 1.53 (2H, m, H_2-5), 1.31 (6H, m, 3 x CH_2), 1.25 (30 H, brs, 15 x CH_2), 0.83 (3 H, t, J = 6.5 Hz, Me-24); ^{13}C NMR ($CDCl_3$): δ 177.22 (C-1), 33.85 (CH_2), 31.97 (C-2), 32.15 (C-3), 29.92 (13 × CH_2), 29.67 (CH_2), 29.58 (CH_2), 29.30 (CH_2), 27.81 (CH_2), 26.27 (CH_2), 24.98 (CH_2), 22.91 (CH_2), 14.33 (Me-24); +ve ESI MS *m/*z (rel. int.): 368 $[M]^+$ ($C_{24}H_{48}O_2$) (2.8).

Lanost-5-en-3α- ol -26-oic acid (3)

Elution of the column with chloroform furnished colourless crystals of **3**, yield 0.24 % ; m. p. 92-93 °C; UV λmax (MeOH): 229 nm; IR υ_{max} (KBr): 3448, 3215, 2928, 2851, 1692, 1635, 1463, 1386, 1275, 1193, 1003, 953 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.25 (1H, m, H-6), 3.22 (1H, dd, J = 4.5, 5.4 Hz, H-3β), 2.33 (1H, m, H-25), 2.29 (2H, m, H_2-7), 2.26 (1H, m, H-9), 2.14 (1H, m, H-17), 2.05 (1H, m, H-20), 1.37 (1H, m, H-8), 2.20 - 1.18 (18 H, m, 9 x CH_2), 1.25 (3H, d, J = 6.5 Hz, Me-27), 1.08 (3H, brs, Me-19), 0.99 (3H, d, J = 6.5 Hz, Me-21), 0.93 (3H, brs, Me-28), 0.87 (3H, brs, Me-30), 0.78 (3H, brs, Me-29), 0.76 (3H, brs, Me-18); ^{13}C NMR (MeOD): δ 34.50 (C-1), 27.23 (C-2), 78.26 (C-3), 42.53 (C-4), 138.81 (C-5), 119.72 (C-6), 29.26 (C-7), 42.05 (C-8), 49.18 (C-9), 38.65 (C-10), 21.09 (C-11), 26.21 (C-12), 48.38 (C-13), 55.06 (C-14), 35.92 (C-15), 48.13 (C-16), 53.27 (C-17), 13.11 (C-18), 20.21 (C-19), 29.74 (C-20), 15.49 (C-21), 35.42 (C-22), 33.96 (C-23), 31.16 (C-24), 29.40 (C-25), 176.89 (C-26), 22.18 (C-27), 24.11 (C-28), 28.03 (C-29), 14.08 (C-30); +ve ESI MS *m/*z (rel. int.): 458 $[M]^+$ ($C_{30}H_{50}O_3$) (5.2), 440 (100), 412 (10.1), 315 (21.2), 297 (41.3).

Lanost-5-en-26-oic acid 3β- olyl palmitate (4)

Further elution of the column with chloroform produced colourless crystals of **4**, yield 167 mg, m. p. 233-235 °C; IR υ_{max} (KBr): 3216, 2923, 2856, 1725, 1690, 1635, 1463, 1388, 1262, 1061, 953, 730 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.35 (1H, m, H-6), 4.19 (1H, dd, J = 5.4, 8.7 Hz, H-3α), 2.32 (2H, t, J = 7.2 Hz, H_2 -2′), 2.24 (1H, m, H-25), 2.21 (2H, m, H_2-7), 2.17 (1H, m, H-9), 2.12 (1H, m, H-17), 2.03 (1H, m, H-20), 1.39 (1H, m, H-8), 2.01 - 1.46 (18 H, m, 9 x CH_2), 1.33 (8 H, brs, 4 x CH_2), 1.28 (18 H, m, 9 x CH_2), 1.25 (3H, d, J = 6.2 Hz, Me-27), 1.02 (3H, brs, Me-19), 0.95 (3H, d, J = 6.3 Hz, Me-21), 0.91 (3H, brs, Me-28), 0.89 (3H, brs, Me-30), 0.84 (3H, t, J = 6.1 Hz, Me-16′), 0.79 (3H, brs, Me-29), 0.74 (3H, brs, Me-18); ^{13}C NMR ($CDCl_3$): δ 34.12 (C-1), 28.02 (C-2), 79.85 (C-3), 43.03 (C-4), 145.34 (C-5), 123.27 (C-6), 29.16 (C-7), 40.92 (C-8), 50.11 (C-9), 38.24 (C-10), 23.87 (C-11), 26.24 (C-12), 47.39 (C-13), 56.89 (C-14), 35.10 (C-15), 39.98 (C-16), 54.50 (C-17), 16.18 (C-18), 19.62 (C-19), 28.91 (C-20), 17.95 (C-21), 34.17 (C-22), 33.21 (C-23), 31.75 (C-24), 28.29 (C-25), 177.63 (C-26), 24.27 (C-27), 21.73 (C-28), 29.91 (C-29), 16.47 (C-30), 166.03 (C-1′), 33.72 (C-2′), 33.21 (C-3′), 30.89 (C-4′), 30.88 (C-5′), 30.88 (C-6′), 30.91 (C-7′), 30.91 (C-8′), 30.75 (C-9′), 30.61 (C-10′), 30.36 (C-11′), 26.24 (C-12′), 25.47 (C-13′), 24.14 (C-14′), 22.68 (C-15′), 14.99 (C-16′); +ve ESI MS *m/z* (rel. int.): 696 $[M]^+$ ($C_{46}H_{80}O_4$) (2.2), 457 (21.6), 440 (100), 297 (14.3), 256 (10.4), 239 (8.6).

Lanostan-3*α*- olyl -26-oic acid 3-O-α-D-glucoside (5)

Elution of the column with chloroform: methanol (19:1) eluants yielded a colourless crystalline mass **5**, yield 0.24%; R_f 0.43 (chloroform: methanol, 1:2); m. p. 192-193°C; UV λ*max* (MeOH): 233 nm; IR υ_{max} (KBr): 3428, 3375, 3260, 2923, 2856, 1690, 1639, 1461, 1383, 1277, 1215, 1171, 1031, 774 cm^{-1}; ^1H NMR (MeOD): δ 3.89 (1H, dd, J = 5.5, 8.9 Hz, H-3α), 2.49 (1H, m, H-25), 2.34 (1H, m, H-9), 2.27 (1H, m, H-5), 2.17 (1H, m, H-17), 2.13 (1H, m, H-20), 2.20 - 1.27 (22 H, m, 11 x CH_2), 1.34 (1H, m, H-8), 1.29 (3H, d, J = 6.3 Hz, Me-27), 1.11 (3H, brs, Me-19), 1.05 (3H, d, J = 6.5 Hz, Me-21), 0.97 (3H, brs, Me-28), 0.90 (3H, brs, Me-30), 0.86 (3H, brs, Me-29), 0.77 (3H, brs, Me-18), 5.24 (1H, d, J = 3.9 Hz, H-1′), 3.99 (1H, m, H-5′), 3.76 (1H, m, H-2′), 3.58 (1H, m, H-3′), 3.54 (1H, m, H-4′), 3.16 (1H, d, J = 5.1 Hz, H_2-6′a), 3.11 (1H, d, J = 4.2 Hz, H_2-6′b); ^{13}C NMR (MeOD): δ 37.79 (C-1), 30.84 (C-2), 80.19 (C-3), 47.36 (C-4), 50.34 (C-5), 22.60 (C-6), 30.55 (C-7), 40.71 (C-8), 48.28 (C-9), 36.68 (C-10), 22.95 (C-11), 28.91 (C-12), 47.52 (C-13), 54.25 (C-14), 34.99 (C-15), 42.83 (C-16), 51.18 (C-17), 18.49 (C-18), 20.46 (C-19), 29.13 (C-20), 17.19 (C-21), 33.15 (C-22), 25.74 (C-23), 31.76 (C-24), 30.23 (C-25), 181.26 (C-26), 24.87 (C-27), 26.14 (C-28), 26.87 (C-29), 15.11 (C-30), 104.86 (C-1′), 74.84 (C-2′), 72.41 (C-3′), 71.65 (C- 4′), 79.70 (C-5′), 64.74 (C-6′); +ve ESI MS *m/z* (rel. int.) : 622 $[M]^+$ ($C_{36}H_{62}O_8$) (9.5), 479 (10.2), 459 (8.5), 443 (2.8), 316 (15.1), 179 (23.1), 163 (18.3), 143 (8.7).

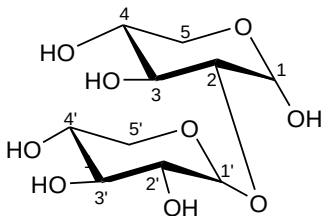
Isolation of a phytoconstituent from the hulls of *Oryza sativa*

***n*-Hexacos-14-enoic acid (6)**

Elution of the column with chloroform produced a colourless semisolid mass of **6**, recrystallized from chloroform - methanol (1:1), yield 139 mg, R_f 0.38 (hexane – ethyl acetate, 7:3); IR υ_{max} (KBr): 3110, 2918, 2863, 1705, 1642, 1439, 1372, 1271, 1062, 865, 721 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.33 (1H, m, $w_{1/2}$ = 8.7 Hz, H-14), 5.31 (1H, m, $w_{1/2}$ = 9.2 Hz, H-15), 2.32 (2H, t, J = 7.3 Hz, H_2-2), 2.04 (2H, m, H_2-13), 1.99 (2H, m, H_2-16), 1.61 (2H, m, H_2 -3), 1.52 (2H, m, H_2-4), 1.25 (4H, m, H_2-5, H_2-6), 1.21 (30H, brs, 15 x CH_2), 0.85 (3H, t, J = 6.5 Hz, Me-26); ^{13}C NMR ($CDCl_3$): δ 180.23 (C-1), 39.18 (C-2), 32.56 (C-3), 31.83 (C-4), 29.16 (C-5), 29.25 (C-6), 29.29 (C-7), 29.33 (C-8), 29.35 (C-9), 29.38 (C-10), 29.41 (C-11), 32.3 (C-12), 33.98 (C-13), 130.22 (C-14), 128.06 (C-15), 37.14 (C-16), 29.21 (C-17), 29.19 (C-18), 29.16 (C-19), 28.79 (C-20), 27.11 (C-21), 25.38 (C-22), 24.55 (C-23), 22.68 (C-24), 33.98 (C-25), 14.15 (C-26); +ve ESI MS *m/z* (rel. int.): 394 $[M]^+$ ($C_{26}H_{50}O_2$) (3.1), 181 (97.2).

RESULTS AND DISCUSSION

Compound **1**, a di-α-L-xyloside, $[M]^+$ at *m/z* 282 ($C_{10}H_{18}O_9$), gave positive tests for glycosides and showed IR absorption bands for hydroxyl groups (3365, 3231 cm^{-1}). The ^1H NMR spectrum of **1** exhibited two one-proton doublets at δ 4.61 (J = 4.8 Hz) and 4.53 (J = 5.7 Hz) assigned to anomeric H-1 and H-1′ protons, respectively, supported the existence of α-glycosidic linkage of the disaccharide unit. The other sugar protons resonated as one-proton multiplets between δ 4.42 - 3.48 and as two-proton doublets at δ 3.31 (J = 4.5 Hz) and 3.20 (J = 4.5 Hz) ascribed to oxymethylene H_2-5 and H_2-5' of the pentose units, respectively. The ^{13}C NMR spectrum of **1** displayed signals for anomeric carbons at δ 99.17 (C-1) and 93.51 (C-1′) and other sugar carbons from δ 79.23 to 70.12. The presence of the sugar H-2 signal in the deshielded region as a one-proton multiplet at δ 4.42 in the ^1H NMR spectrum and C-2 carbon signal at δ 79.23 in the ^{13}C NMR spectrum suggested (2→1′) linkage of the sugar units. Acid hydrolysis of **1** yielded D-xylose, R_f 0.81 (*n*-butonal – pyridine – water, 6 : 4 : 3, *v/v*), m. p. 153 - 156 °C, $[\alpha]_D$20 + 91 ° (water, 10%). On the basis of these evidences the structure of **1** has been formulated as α-L-xylopyranosyl-(2→1')-α-L-xylopyranoside, a new dixyloside from the leaves of *Carya illinoinesis* (Fig. 1).



α-L-Xylopyranosyl-(2→1')-α-L-xylopyranoside **(1)**

Fig 1: Structural formula of the chemical constituent 1 isolated from the leaves of *Carya illinoinesis.*

Compound **2** was a known long chain saturated fatty acid identified as *n*-tetracosanoic acid (lignoceric acid).[57] (Fig. 2)

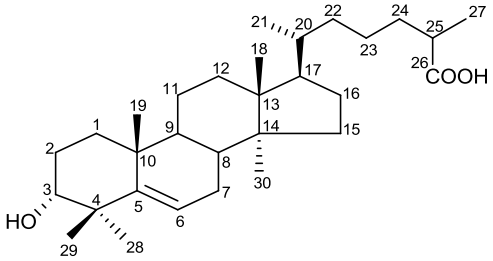
Compound **3** gave positive Liebermann-Buchardt[58] and effervescences with sodium bicarbonate solution indicating the presence of a carboxylic function in the molecule. Its IR spectrum displayed characteristic absorption bands for a hydroxyl group (3448 cm^{-1}), carboxylic group (3215, 1692 cm^{-1}) and unsaturation (1635 cm^{-1}). On the basis of mass and ^{13}C NMR spectra, its molecular weight was established at *m/z* 458 consistent with the molecular formula of a triterpenic acid, $C_{30}H_{50}O_3$. The ion peaks arising at *m/z* 440 [M - H_2O]$^+$ and 412 [M - HCOOH]$^+$ indicated the presence of one each hydroxy and carboxylic functions in the molecule. The ion fragments generated at *m/z* 315 [M – side chain, $C_8H_{15}O_2$]$^+$ and 297 [315 – H_2O]$^+$ suggested the existence of the carboxylic function in the side chain and hydroxyl group and vinylic linkage in the carbocyclic ring structure. The hydroxyl group was placed at C-3 on the basis of biogenetic consideration. The ^{1}H NMR spectrum of **3** exhibited a one-proton multiplet at δ 5.25 assigned to vinylic H-6 proton, a one-proton double doublet at δ 3.22 (J = 4.5, 5.4 Hz) ascribed to β-oriented carbinol H-3 proton, five three-proton broad singlets at δ 1.08, 0.93, 0.87, 0.78 and 0.76 due to tertiary C-19, C-28, C-30, C-29 and C-18 methyl protons, respectively, and as two three-proton doublets at δ 1.25 (J = 6.5 Hz) and 0.99 (J = 6.5 Hz) associated correspondingly with secondary C-27 and C-21 methyl protons. The presence of methyl groups attached to saturated carbons in the range δ 1.25–0.76 supported the lanostene-type skeleton. The remaining methine and methylene protons appeared as one-proton multiplets at δ 2.33 (H-25), 2.26 (H-9), 2.14 (H-17), 2.05 (H-20) and 1.37 (H-8) as two-proton multiplets between δ 2.29 - 1.18 due to methylene protons. The ^{13}C NMR spectrum of **3** displayed signals for vinylic carbons at δ 138.81 (C-5) and 119.72 (C-6), carbinol carbon at δ 78.26 (C-3), carboxylic carbon at δ 176.89 (C-26) and methyl carbons from δ 28.03 to 13.11. The ^{1}H and ^{13}C NMR spectral data of the triterpenic unit of **2** were compared with the reported spectral data of lanostene-type triterpenoids.[58,59] On the basis of these evidences the structure of **3** was established as lanost-5-en-3α-ol 26-oic acid, a new lanostenoic acid (Fig. 2).

Compound **4**, named lanost-5-en-26-oic acid 3β-olyl palmitate, responded positively to Liebermann-Burchardt test for triterpenoids[58] and showed IR absorption bands for carboxylic group (3216, 1690 cm^{-1}), ester function (1725 cm^{-1}), unsaturation (1635 cm^{-1}) and long aliphatic chain (730 cm^{-1}). On the basis of mass and ^{13}C NMR spectra the molecular ion peak of **4** was determined at *m/*z 696 consistent with a molecular formula of a lanostanyl ester, $C_{46}H_{80}O_4$. The ion fragments arising at *m/*z 440 [C_3 - O fission, $C_{30}H_{49}O_2$]$^+$, 457 [$C_{1'}$ - O fission, $C_{30}H_{49}O_3$]$^+$, 256 [M – 440, $CH_3(CH_2)_{14}COO$]$^+$, 239 [M – 457, $CH_3(CH_2)_{14}CO$]$^+$ and 297 [440 – side chain, $C_8H_{15}O_2$]$^+$ indicated the attachment of a palmityl group linked to the lanostenoic acid unit possessing a C_8 side chain with a carboxylic function. The ^{1}H NMR spectrum of **4** showed a one-proton multiplet at δ 5.35 assigned to vinylic H-6 proton, a one-proton double doublet at δ 4.38 with coupling interactions of 5.4 and 8.7 Hz attributed to oxymethine H-3α proton, two three-proton doublets at δ 1.25 (J = 6.2 Hz) and 0.95 (J = 6.3 Hz) ascribed to secondary C-27 and C-21 methyl protons, respectively, five three-proton broad singlets at δ 1.02 (Me-19), 0.91 (Me-28), 0.89 (Me-30), 0.79 (Me-29) and 0.74 (Me-18) accounted to tertiary methyl protons and a three-proton triplet at δ 0.84 (J = 6.1 Hz) ascribed to primary C-16′ methyl protons. The remaining methylene and methine protons resonated as a two-proton triplet δ 2.32 (J = 7.2 Hz) due to methylene H_2 -2′ protons adjacent to the ester function, as multiplets between δ 2.24 – 1.46 and as broad singlets at δ 1.33 (8 H) and 1.28 (18 H). The ^{13}C NMR spectrum of **4** showed signals for ester carbon at δ 166.03 (C-1′), vinylic carbons at δ 145.34 (C-5) and 123.27 (C-6), oxymethine carbon at δ 79.85 (C-3), carboxylic carbon at δ 177.63 (C-26) and methyl carbons from δ 29.91 to 14.99. The ^{1}H and ^{13}C NMR spectral data of the triterpenic unit of **4** were compared with the reported data of lanostene-type triterpenoids.[58,59] Acid hydrolysis of **4** yielded palmitic acid, m. p. 62 – 63 °C, R_f : 0.30 (85% glacial acetic acid). On the basis of above discussion the structure of **4** has been elucidated as lanost-5-en-3β-olyl hexadecanoate, a new lanostane type-triterpenic ester (Fig 2).

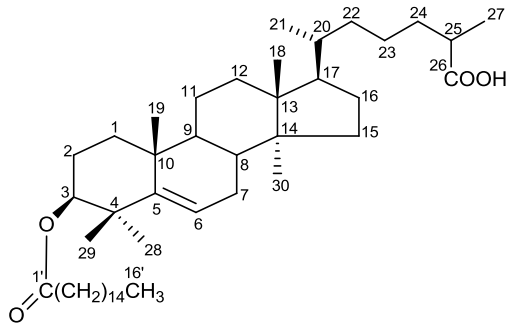
Compound **5,** named lanostan-3α- olyl -26-oic acid 3-O-α-D-glucoside, gave positive tests for glycosides, effervescence with sodium bicarbonate solution and showed characteristics IR absorption bands for hydroxyl groups (3428, 3375 cm^{-1}), carboxylic function (3260, 1690 cm^{-1}) and unsaturation (1639 cm^{-1}). On the basis of mass and ^{13}C NMR spectra, the molecular ion peak of **5** was determined at *m/z* 622 corresponding to the molecular formula of a tetracyclic triterpenic monoglycoside, $C_{36}H_{62}O_8$. The ion fragments arising at *m/z* 143 [C_{17} – C_{20} fission, side chain $C_8H_{15}O_2$]$^+$ and 479 [M – 143]$^+$ indicated the presence of the carboxylic group in the side chain. The ion peaks generated at *m/z* 163 [$C_6H_{11}O_5$]$^+$, 179 [$C_6H_{11}O_6$]$^+$, 459 [M – 163]$^+$, 316 [459 – 143]$^+$ and 443 [M – 179]$^+$ suggested the existence of an hexose unit linked with the triperpenic unit. The ^{1}H NMR spectrum of **5** showed a one- proton double doublet at δ 3.89 (J = 5.5, 8.9 Hz) assigned to α-oriented oxymethine H-3 proton, two three-proton doublets at δ 1.29 (J = 6.3 Hz) and 1.05 (J = 6.5 Hz) ascribed to secondary C-27 and C-21 methyl protons, respectively, five three-proton singlets at δ 1.11, 0.97, 0.90, 0.86 and 0.77 attributed correspondingly to C-19, C-21, C-28, C-30, C-29 and C-18 tertiary methyl protons and the remaining methine and methylene protons between δ 2.34 – 1.34. A one-proton doublet at δ 5.24 (J = 3.9 Hz) was accounted to α-oriented anomeric H-1′ proton. Two one-proton doublets at δ 3.16 (J = 5.1 Hz) and 3.11 (J = 4.2 Hz) were due to hydroxymethylene H_2-6 protons.

The other sugar oxymethine protons resonated as one-proton multiplets at δ 3.99 (H-5′), 3.76 (H-2′), 3.58 (H-3′) and 3.54 (H-4′). The ^{13}C NMR spectrum of **5** showed important signals for oxymethine carbon at δ 80.19 (C-3), carboxylic carbon at δ 181.26 (C-26), methyl carbons between δ 26.14 – 15.11, anomeric carbons at δ 104.86 (C-1′), other sugar carbons from δ 79.70 to 64.74 and the remaining methylene and methine carbons between δ 54.25 - 22.60. The ^{1}H NMR and ^{13}C NMR spectral data of the triterpenic nucleus were compared with other lanostene –type molecules [58, 59]. Acid hydrolysis of **5** yielded α-D-glucose acid, R_f 0.78 (*n*-butonal- acetic acid-water, 4:1:1.6), specific rotation, $[\alpha]^{D}_{25^{o}}$ +112º (water). On the basis of spectral data analysis and chemical reactions, the structure of **5** has been characterized as lanostan-3α- olyl -26-oic acid 3-O-α-D-glucopyranoside, a new lanostanoic acid glucoside (Fig. 2).

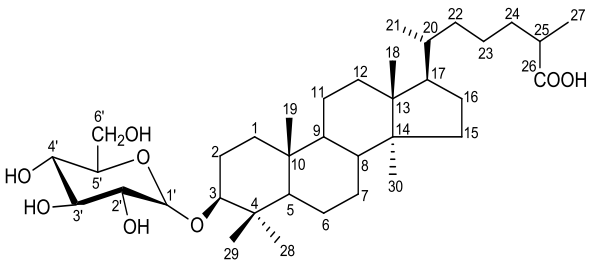
Lignoceric acid **(2)**



Lanostan-5-en-3α-ol-26-oic acid (**3**)



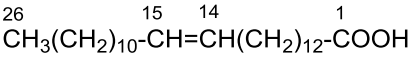
Lanostan-5-en-26-oic acid-3β-olyl palmitate **(4)**



Lanostan-3α- olyl -26-oic acid 3-O-α-D-glucoside (**5**)

Fig 2: Structural formulae of the chemical constituents 2 – 5 isolated from the aerial parts of *Helichrysum stoechas*.

Compound **6** was a known unsaturated fatty acid formulated as *n*-hexacos-14-enoic acid (Fig. 3)[60].



n-Hexacosa-14-enoic acid **(6)**

Fig 3: Structural formula of the chemical constituent 6 isolated from the hulls of *Oryza sativa.*

CONCLUSION

Phytochemical investigation of the leaves *C. illinoinensis* gave a new dixyloside characterized as α-L-xylopyranosyl-(2→1')-α-L-xylopyranoside (**1**). The aerial parts of *H. stoechas* afforded *n*-tetracosanoic acid (lignoceric acid, **2**), lanost-5-en-3α-ol 26-oic acid (**3**), lanost-5-en-3β-olyl hexadecanoate (lanost-5-en-26-oic acid 3β-olyl palmitate, **4**) and lanostan-3α- olyl -26-oic acid 3-O-α-D-glucopyranoside (lanostan-3α- olyl -26-oic acid 3-O-α-D-glucoside, **5**). The hulls of *O. sativa* led to the isolation of an aliphatic acid identified as *n*-hexacos-14-enoic acid (**6**). This work has enhanced understanding about the phytoconstituents of these plants. These secondary metabolites can be used as analytical markers for quality control of these herbal drugs and their traditional formulations.

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